Journal of Organometallic Chemistry 880 (2019) 47–55

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Half–Sandwich (η^6–*p*–Cymene) Ruthenium(II) complexes bearing 5–Amino–1–Methyl–3–Phenylpyrazole Schiff base ligands: Synthesis, structure and catalytic transfer hydrogenation of ketones

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ARTICLE INFO

Article history:
Received 10 October 2018
Received in revised form
23 October 2018
Accepted 30 October 2018
Available online 2 November 2018

Keywords:
p–
Cymene ruthenium(II) complexes
Schiff base ligands
characterization
Crystal structure
Catalytic transfer hydrogenation

ABSTRACT

New (η^6–*p*–cymene) ruthenium(II) complexes containing Schiff base ligands of the general composition [RuCl(η^6–*p*–cymene)(L_{1-3})] have been synthesized. The complexes were characterized by analytical and spectral (FT–IR, UV–Vis, ^{1}H NMR and ^{13}C NMR) methods. The molecular structure of the representative complex [RuCl(η^6–*p*–cymene)(L_3)] **6** was determined by single crystal X–ray diffraction studies, revealing a pseudo-octahedral piano stool geometry around ruthenium(II) ion. Further, one of the complexes **6** was screened for their efficiency as a catalyst in the transfer hydrogenation of various ketones to alcohols in the presence of KOH and 2–propanol showed an excellent conversion up to 99%. Under the optimized conditions, the influence of base, reaction temperature and substrate scope was also reported.

1. Introduction

Half-sandwich ruthenium(II) arene complexes offer a versatile platform for the design and synthesis of novel compounds with potential applications in catalysis and medicinal and supramolecular chemistry. Particularly, half-sandwich ruthenium(II) Schiff base complexes are used as highly efficient transition metal homogeneous catalysts for the synthesis of valuable organic compounds [1–3]. In the area of metal complexes catalyzed transformations, bidentate O, N donor based ligands are playing an important role because of their ability to form complexes with several metals in different oxidation states. Schiff base compounds are useful chelating ligands which are readily modifiable to allow fine-tuning of steric and electronic properties of the ruthenium complex [4]. Exploring the reactivity of half-sandwich ruthenium complexes with Schiff base ligands would therefore be interesting. These ruthenium complexes have attracted a lot of interest due to their catalytic activity in a wide range of organic reactions [5–14]. Since last decade, a variety of half sandwich ruthenium complexes have been extensively studied in transfer hydrogenation reactions [15]. Under basic conditions and mainly with *i*–PrOH as the solvent, ruthenium(II) complexes bearing arene, PP, NN, NO, or NPN ligands have been investigated for transfer hydrogenation reactions [16].

Ruthenium complexes are preferable for transfer hydrogenation reaction than those of rhodium and iridium because of their high activity and lower cost. Among the various ruthenium complexes, arene ruthenium complexes belong to a well-established family of metal complexes played an important role in the development of organometallic chemistry. Noyori and co-workers have documented N-tosylethylenediamine or β-amino alcohol ligands exhibited efficient catalytic activity in the transfer hydrogenation of ketones and imines [17]. New 2–(2–pyridyl–2–ol)–1,10-phenanthroline based ruthenium complexes have been reported as highly active catalysts for reduction of ketones in the presence of 2-propanol at 80 °C [18]. Recently, Ramesh et al. have reported arene Ru(II) hydrozone complexes as catalysts for transfer hydrogenation ketones with low catalyst loading in 5 h [19].

Remarkably, Baratta et al. have developed arene-free ruthenium catalysts which are extremely active in the transfer hydrogenation of acetophenone with NaOH as the base [20]. Ruthenium complexes containing different types of ligands such as arylazo ligands [21], Schiff base ligands [22] and 2, 2′–bipyridine ligand [23] are considered to be the most active catalysts for transfer

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https://doi.org/10.1016/j.jorganchem.2018.10.029
0022-328X/

hydrogenation reaction in the presence of a base. In order to design new ruthenium(II) complexes with potential catalytic activity in the reduction of ketones, we decided to synthesize the half-sandwich ruthenium(II) Schiff base complexes.

Herein, we report the synthesis of (η^6–*p*–cymene) ruthenium(II) complexes containing bi-dentate Schiff base ligands along with transfer hydrogenation of a series of ketones. The synthesized complexes have been characterized by elemental analysis and spectroscopy (FT–IR, UV–Vis, ^{1}H NMR and ^{13}C NMR) techniques. The molecular structure of complex **6** was confirmed by single crystal X–ray diffraction. Further, one of the half-sandwich ruthenium(II) Schiff base complexes was employed as catalyst for promoting a variety of ketones to corresponding secondary alcohols in the presence of 2–propanol and KOH.

2. Results and discussion

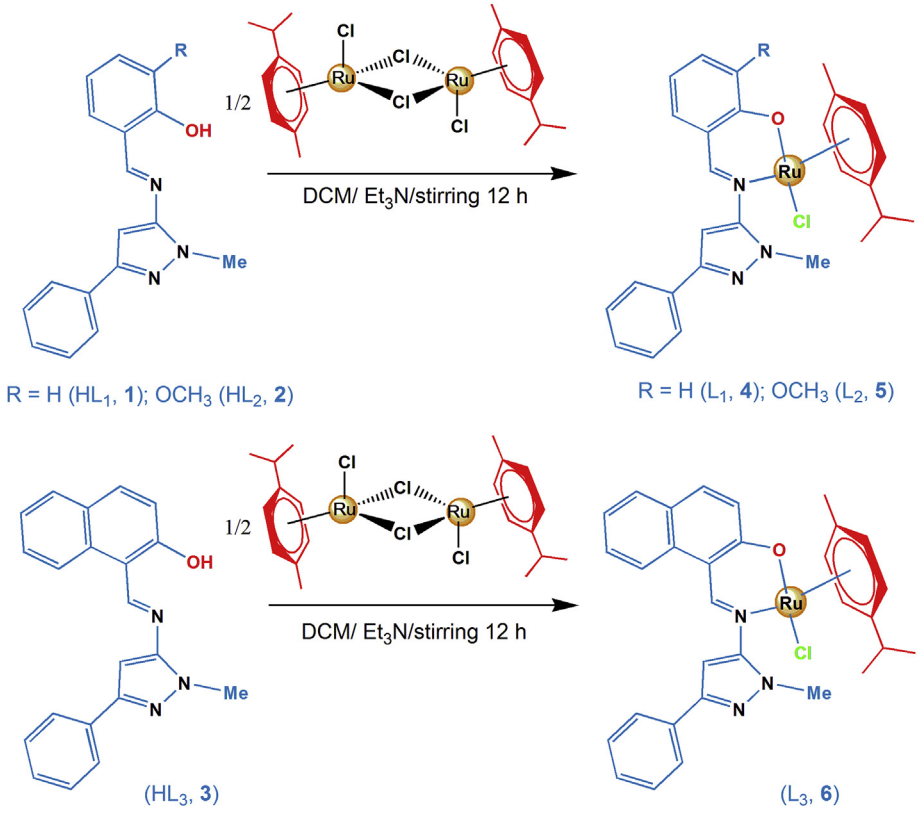
2.1. Synthesis and spectroscopic study

The Schiff base ligands (HL_1–HL_3) **1**–**3** were readily synthesized from the condensation of the 5–amino–1–methyl–3–phenyl-pyrazole with corresponding aldehyde and its derivatives respectively. The orange half-sandwich ruthenium complexes **4**–**6** were obtained by reaction of [(η^6–*p*–cymene)Ru(μ–Cl)Cl]$_2$ with two equivalent Schiff base ligands in the presence of Et_3N in CH_2Cl_2 under stirring at room temperature for 12 h (Scheme 1). The ruthenium complexes were isolated as pure complexes by chromatography silica gel using EtOAc/petroleum ether as an eluent to yield of 60–80%. All the complexes have been characterized by FT–IR, UV–Vis, ^{1}H NMR and ^{13}C NMR spectroscopy. The half-sandwich ruthenium complexes are air and moisture stable, soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, C_6H_6, DMSO, CH_3OH and C_2H_5OH solvents.

An infrared red spectrum helps in determining the coordination mode of ligand with metal ion. The Free ligands **1**–**3** exhibit a broad band in the region 3320–3399 cm^{-1}, which is characteristic of the ν(OH) functional group [24]. The azomethine ν(C=N) and the ν(C–O) stretching frequencies are assigned in the region around 1612–1620 cm^{-1} and 1270–1296 cm^{-1} respectively [24–27]. Upon coordination the frequencies of the azomethine ν(C=N) stretching shift toward lower frequencies at 1600–1605 cm^{-1} and phenolic ν(C–O) stretching exhibit slightly higher frequencies at 1320–1331 cm^{-1} as compared to their respective ligands. Thus, the imine nitrogen and phenolic oxygen functionalities suggests the presence of a pseudo octahedral environment around ruthenium(II) metal centre [28,29].

The electronic spectra of the half-sandwich ruthenium(II) Schiff base complexes in chloroform exhibited very intense bands around 300–330 nm and 340–380 nm, which are assigned to the ligand-centered (LC) π–π* and n–π* transitions, respectively. The representative UV–Vis spectra of complexes **4**–**6** are given in Fig. 1. The lowest energy absorption bands in the electronic spectra of the complexes in the visible region 450–480 nm are ascribed to MLCT (metal to ligand charge transfer) transitions [30–32].

The ^{1}H NMR spectra of all the ligands and complexes were recorded in $CDCl_3$ to confirm the coordination mode of the Schiff base ligand to the ruthenium(II) ion. The Schiff base ligands (HL_1–HL_3) shows a singlet in the δ 12.37–14.29 ppm range can be attributed to the proton of the –OH group [33]. The azomethine proton (CH=N) was observed as a singlet at δ 8.73–9.60 ppm for the ligands HL_1 to HL_3 respectively. The multiplets of the aromatic protons of the ligands were in the region of δ 6.59–8.22 ppm. The pyrazole CH proton appears as a singlet in the range 6.59–6.61 ppm. A sharp singlet at δ 3.88–4.01 ppm in the spectra of ligand was attributed to methyl and methoxy groups respectively.



Scheme 1. Synthesis of half sandwich (η^6–*p*–cymene) ruthenium(II) Schiff base complexes.

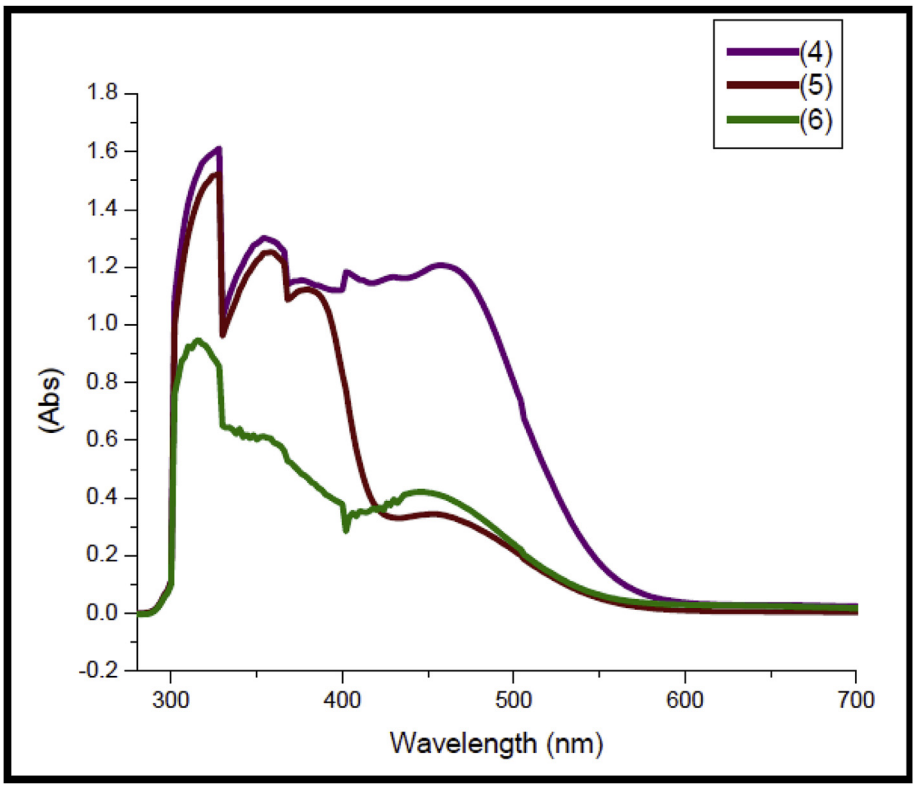


Fig. 1. Electronic spectrum of [Ru(η^6–*p*–cymene)(Cl)($L_{4–6}$)].

The singlet due to the –OH proton of the free ligand in the region δ 12.37–14.29 ppm is absent in the complexes, **4**–**6** supporting the coordination of the phenolate oxygen to the Ru(II) ion. The imine proton (CH=N) of the complexes was observed as a singlet in the region δ 8.52–8.81 ppm. In all the complexes, the four aromatic hydrogens of *p*-cymene protons appear in the region of δ 3.98–5.40 ppm. Additionally, the methyl group of the *p*-cymene comes as a singlet around the region of δ 2.15–2.22 ppm. The isopropyl methyl protons of the *p*–cymene appeared as two sets of doublets in the region of δ 1.17–1.26 ppm. Further, the isopropyl CH protons come in the region of δ 2.81–2.92 ppm as septet [34–36]. The representative ^{1}H NMR and ^{13}C NMR spectra of the ligands and complexes are shown in Figs. S1–S9 (supporting information).

2.2. Crystal structure

Single crystal X–ray diffraction analysis of the ligand and complex was performed to confirm the structure of these complexes. The ORTEP view of ligand **2** and complex **6** is shown in Figs. 2 and 3 and packing arrangement is given in Fig. 4. The summary of single crystal X–ray structure refinement is shown in Table 1 and selected bond parameters are listed in Table 2. The complex crystallizes in the monoclinic space group C 2/c. The coordination geometry of the ruthenium atoms is the classic three-legged piano-stool arrangement with a pseudo–octahedral geometry. The ruthenium centers have six-coordinate geometry assuming that the Schiff base ligand, a chloro group and the centroid of the aromatic ring of the *p*–cymene ring serve as a three-coordinated ligand, which is common for half sandwich "piano-stool" structures [37–45]. The Schiff base ligand binds to ruthenium metal centre *via* O, N atom forming six membered ring bite angels of 86.28(11)° O(1)–Ru(1)–N(3), 85.00(10)° O(1)–Ru(1)–Cl(1), 86.06(9)° N(3)–Ru(1)–Cl(1) and 120.5(4)° N(1)–C(1)–N(3). The Ru–C distances are (2.157(4), 2.191(4), 2.212(4), 2.204(3), 2.182(3) and 2.13–2.21 Å) typically found for *p*–cymene coordinated ruthenium centre [35,36]. The bond distances around the ruthenium atom vary over a small range Ru(1)–O(1) 2.057(3) Å, Ru(1)–N(3) 2.096(3) Å and N(1)–N(3) 1.353(5) Å which was in good agreement with other related *p*–cymene ruthenium complexes containing [ON] anionic bidentate ligands [46–49].

2.3. Catalytic transfer hydrogenation of ketones

To evaluate the usefulness of synthesized *p*-cymene ruthenium(II) Schiff base complexes, we investigated the catalytic application of the complex catalyst **4**–**6** to the transfer hydrogenation of various ketones. The catalytic reactions were performed using (5.0 mmol) of benzophenone as model substrate, 0.2 mol% of complexes **4**–**6** and KOH (0.03 mmol) in 2–propanol were refluxed for 3 h. All the complexes were found to be effective catalysts affording conversions 80%, 84% and 95% respectively and the results are summarized in Table 3.

2.4. Effect of catalyst/substrate ratio and base variation study

The catalyst **6** was chosen for the subsequent reaction because it showed the highest conversion. In order to optimize the reaction conditions, different catalyst and substrate ratios were tested and the results are summarized in Table 4. Benzophenone was selected as a test-substrate and allowed it to react in 2–propanol with catalytic quantities of complex **6** in the presence of KOH. The reaction proceeds with high yield of benzophenone to benzhydrol when a C: S ratio of 1:500 (0.2 mol %) is used. When increasing the C/S ratios to 1:1000, 1:1500, and 1:2000, the reaction proceeds with lower conversion. Thus, it was concluded that catalyst and substrate ratio of 1:500 is the best compromise between optimal reaction rates in

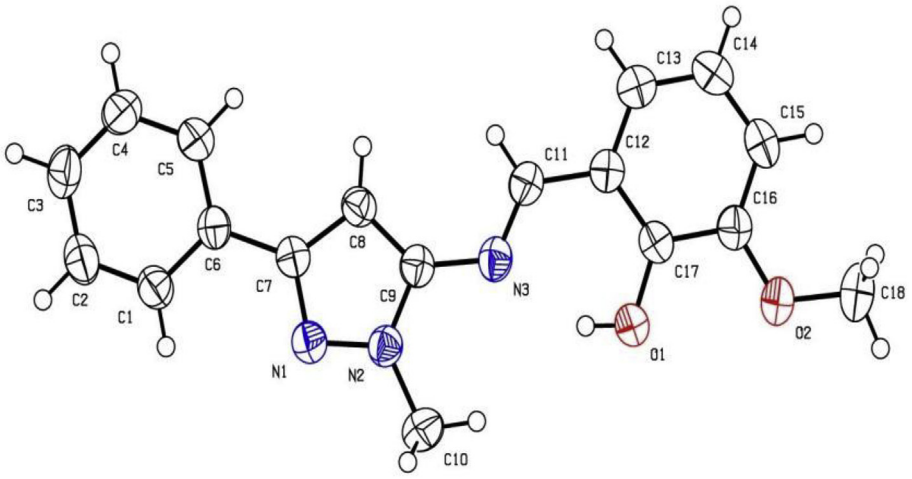


Fig. 2. ORTEP diagram of the $\mathbf{HL_2}$ (**2**); ellipsoids are drawn at the 50% probability level.

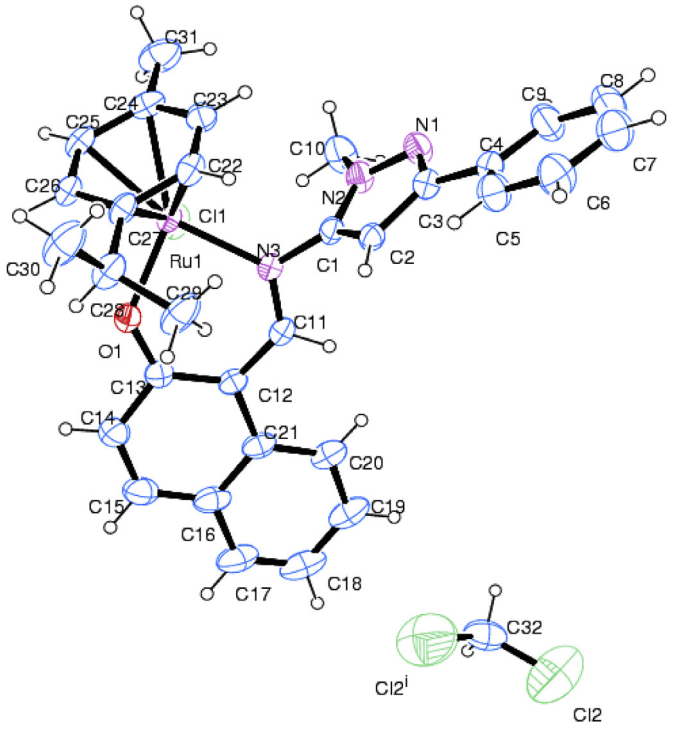


Fig. 3. ORTEP diagram of the complex [Ru(η^6–*p*–cymene)Cl(L_3)] (**6**); ellipsoids are drawn at the 50% probability level.

2–propanol.

Further, in order to improve the reaction conditions such as base and reaction temperature, the transfer hydrogenation reaction was carried out the reaction using benzophenone as substrate and complex **6** as a test catalyst in the presence of 2–propanol with various bases. The reaction rates were found to be strongly dependent on the base employed and a variety of base was screened. A remarkable increase in the product formation was observed in presence of strong inorganic bases like KOH or NaOH which gives higher conversions of 95% and 89%, respectively. Whereas weak inorganic bases such as Na_2CO_3 and K_2CO_3 gives moderate conversions of 60% and 58%, respectively. For organic bases such as Et_3N and pyridine we observed only trace amounts of alcohol were formed. The conversions are summarized in Table 4. Therefore, the activity trend is found to be in the order KOH > NaOH > Na_2CO_3 > K_2CO_3> Et_3N > pyridine, consistent with the relative strength of the bases.

2.5. Transfer hydrogenation of ketones

The catalytic transfer hydrogenation of ketones to alcohols in the presence of half sandwich ruthenium(II) Schiff base complexes has been studied in isopropanol and KOH as a base. Several aromatic, cyclic and aliphatic ketones were carried out with complex **6** and the results are summarized in Table 5. The complex catalyzes transfer hydrogenation of acetophenone with substituents of varying electronic properties were efficiently reduced to the corresponding secondary alcohols with good to excellent conversions in all the cases over a period of 3 h. The catalytic reduction of acetophenone into 1–phenyl ethanol is obtained about 99%. Sterically hindered ketones such as benzophenone to their corresponding secondary alcohol had good conversion about 95%. The electron donating substituent present in the substrates observed to have slightly less activity in the reduction of ketones. In case of 4–methyl acetophenone and 4–methoxy acetophenone (entries 3 and 4) conversions to their corresponding alcohols are 83% and 80% respectively. The electron withdrawing substituent present in the substrates found to play a significant role in the conversion of ketone to alcohols. Substrate with electron withdrawing substituents such as Cl, Br and NO_2 (entries 5, 6 and 7) gave excellent conversions of 93%, 96% and 98% respectively. Cyclic ketones containing five six membered rings (entries 8 and 9) were reduced effectively to give the corresponding alcohols with conversions of up to 92% and 94%. The complex catalyst also efficiently catalyzed the reduction of aliphatic ketones such as 2–butanone, 2–pentanone, diethyl ketone and 4–methylpentan–2–one (entries 10 to 13) to their corresponding secondary alcohols having 92%, 98%, 99% and 93% respectively. Acetone was identified as the only by–product in all the cases.

It is worth to note that the observed results are significantly better than those previously reported [50–52]. The advantage of the present catalytic system is the use of low catalyst loading and less time. Further, the enhancement of the catalytic activity of the present complexes is may be due to the unsymmetrical environment around the metal centre by the steric and electronic nature of bidentate Schiff base ligands. In addition, the ease by which these catalysts are prepared offers another important advantage. The

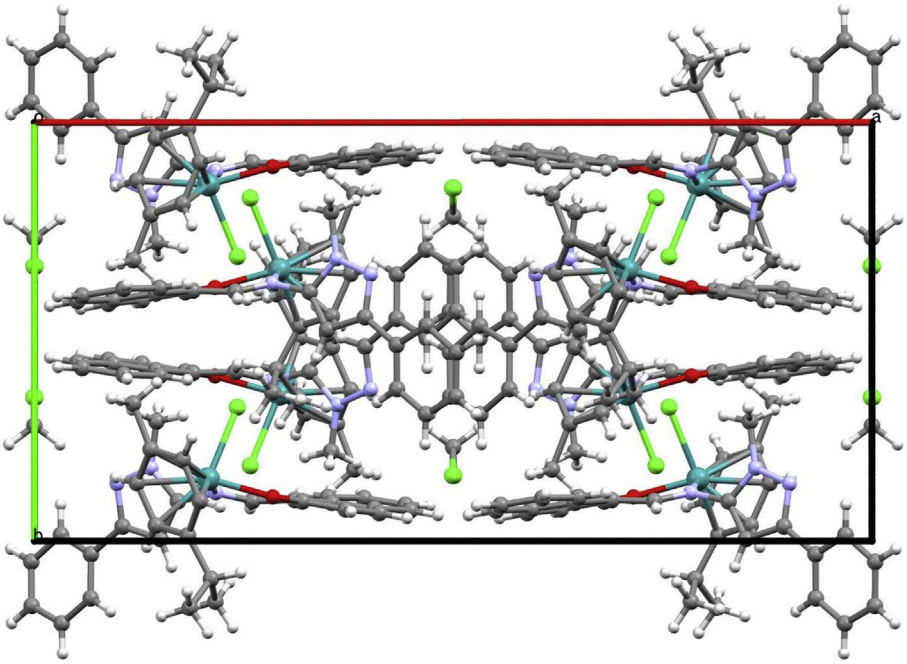


Fig. 4. Packing diagram of complex **6**.

Table 1
Crystal data and structure refinement for ligand **HL_2** and complex **6**.

HL_2			6	
Empirical formula	C_{18} H_{17} N_3 O_2		C_{63} H_{62} Cl_4 N_6 O_2 Ru_2	
Formula weight	307.35		1279.12	
Temperature	296(2) K		296(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Orthorhombic		Monoclinic	
Space group	P 212121		C 2/c	
Unit cell dimensions	a = 6.3165(4) Å	α = 90°	a = 26.3384(10) Å α = 90°.	α = 90°.
	b = 12.8242(5) Å	β = 90°.	b = 12.8242(5) Å	β = 103.131(2)°
	c = 29.1434(17) Å	γ = 90°	c = 17.4790(6) Å	γ = 90°
Volume	1561.09(16) $Å^3$		5749.5(4) $Å^3$	
Z	4		4	
Density (calculated)	1.308 Mg/m^3		1.478 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}		0.761 mm^{-1}	
F(000)	648		2616	
Crystal size	0.22 × 0.14 × 0.08 mm^3		0.350 × 0.300 × 0.220 mm^3	
Theta range for data collection	1.397–29.016°		2.887–29.274°	
Index ranges	−8 ≤ h<=8, −11 ≤ k<=11, −39 ≤ l<=39		−36 ≤ h<=35, −16 ≤ k<=17, −23 ≤ l<=23	
Reflections collected	9225 27948			
Independent reflections	4175 [R(int) = 0.0210]		7667 [R(int) = 0.0514]	
Completeness to theta = 25.242°	99.4%		99.3%	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data/restraints/parameters	3945/0/208		7667/0/353	
Goodness-of-fit on F^2	1.076		1.073	
Final R indices [I > 2sigma(I)]	R_1 = 0.0463, wR_2 = 0.1170		R_1 = 0.0546, wR_2 = 0.1295	
R indices (all data)	R_1 = 0.0596, wR_2 = 0.1325		R_1 = 0.0902, wR_2 = 0.1464	
Extinction coefficient	n/a		0.0022(2)	
Largest diff. peak and hole	0.213 and −0.220 e.$Å^{-3}$		0.615 and −0.706 e.$Å^{-3}$	

work up process is very simple for this catalytic system, as the catalyst is stable in all organic solvents. Though the mechanistic aspect of the reaction was not studied, it is believed that the transfer hydrogenation proceeded through Ru–H intermediate, which was already proved by several research groups [53]. The formation of Ru–iso–propoxide species which undergoes β-hydride elimination leads to form ruthenium metal hydride species with the release of acetone. Insertion of ketone to Ru–H species, resulting in the secondary alkoxide which involves alcohol metathesis to give the alcoholic product and regenerate the original catalyst.

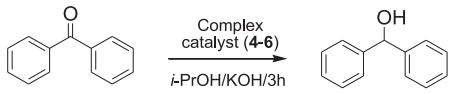
3. Conclusion

In summary, new air stable half-sandwich (η^6–*p*–cymene) ruthenium(II) Schiff base complexes of the type [Ru(η^6–*p*–cymene)(Cl)(L_{1-3})] with O, N chelating ligands have been synthesized. The characterization of all the complexes accomplished by

Table 2
Selected bond angle (°) and length (Å) for Ligand **HL_2** and complex **6**.

HL_2		6	
Bond angle (°)			
N(1)–N(2)–C(10)	119.9(2)	N(2)–C(1)–N(3)	120.5(4)
N(1)–N(2)–C(9)	111.9(2)	N(1)–C(3)–C(2)	120.4(4)
N(2)–N(1)–C(7)	105.0(2)	N(1)–C(3)–C(4)	120.4(4)
N(1)–C(7)–C(6)	120.3(2)	O(1)–Ru(1)–C(25)	109.32(14)
O(1)–C(17)–C(12)	122.9(2)	N(3)–Ru(1)–Cl(1)	86.06(9)
N(3)–C(11)–C(12)	122.7(2)	O(1)–Ru(1)–N(3)	86.28(11)
		O(1)–Ru(1)–Cl(1)	85.00(10)
Bond Length (Å)			
N(1)–C(7)	1.341(3)	Ru(1)–Cl(1)	2.430(11)
N(2)–N(1)	1.347(3)	Ru(1)–O(1)	2.057(5)
N(3)–C(9)	1.388(3)	Ru(1)–N(3)	2.096(3)
N(3)–C(11)	1.285(3)	N(1)–N(2)	1.353(5)
C(17)–O(1)	1.345(3)	C(13)–O(1)	1.293(4)
C(16)–O(2)	1.368(3)	C(10)–N(2)	1.448(6)
		C(1)–N(2)	1.359(5)
		C(1)–N(3)	1.421(4)

Table 3
Catalytic activity of the complexes **4**–**6**.[a]

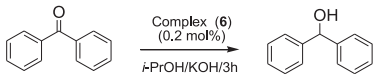


Entry	Complex	Conversion[b] (%)
1	**4**	80
2	**5**	84
3	**6**	95

[a] Reaction conditions: reactions were carried out at 80 °C using benzophenone (5.0 mmol), catalyst (0.01 mmol), base (0.03 mmol) and *i*–PrOH (5 mL).
[b] Conversion was monitored by GC analysis and are average of two runs.

analytical and spectral (FT–IR, UV–Vis, ^{1}H NMR and ^{13}C NMR) methods. The molecular structure of one of the complex **6** was confirmed by the single crystal X–ray diffraction method which reveals Schiff base ligand coordinate to ruthenium *via* O, N donor and indicates the presence of pseudo-octahedral geometry. The catalytic efficiency of one of the complexes **6** were developed in transfer hydrogenation reaction and was found to be an excellent catalyst among the series in the conversion of ketones to alcohols with maximum conversion of 99%.

Table 4
Effect of catalyst/substrate ratio and base by [Ru(η^6–*p*–cymene)(Cl)(L_3)] **6**.[a]



Entry	C/S ratio	Base	Time (h)	Conversion[b] (%)
1	1:500	KOH	3	95
2	1:1000 KOH	3	82	
3	1:1500	KOH	3	76
4	1:2000	KOH	3	60
5	1:500	–	3	0
6	500	KOH	3	0[c]
7	1:500	NaOH	3	89
8	1:500	Na_2CO_3	10	60
9	1:500	K2CO3	10	58
10	1:500	Et3N	12	Trace
11	1:500	Pyridine	12	Trace

[a] Reaction conditions: reactions were carried out at 80 °C using benzophenone (5.0 mmol), catalyst (0.01 mmol), base (0.03 mmol), *i*-PrOH (5 mL).
[b] Conversion was monitored by GC analysis and are average of two runs.
[c] Reaction carried out in the absence of catalyst.

4. Experimental section

4.1. Reagents and materials

Commercial $RuCl_3.3H_2O$ was purchased from Himedia Pvt. Ltd. The solvents were purified and dried according to standard procedures [54]. 5–amino–1–methyl–3–phenyl pyrazole, salicylaldehyde, 2–hydroxy–3–methoxy benzaldehyde and 2–hydroxy–1–naphthaldehyde were obtained from Aldrich. The starting precursor complex [(η^6–*p*–cymene)Ru(μ–Cl)Cl]$_2$ [55] was prepared according to the reported procedure.

4.2. Physical measurements

Microanalytical (C, H, N) data were obtained with a Vario EL III Elemental analyzer at SAIF–Cochin. Melting Points were recorded in the Boetius micro heating table and are uncorrected. The FT–IR spectra of the compounds were recorded in Agilent Resolution pro system spectrometer over the range 4000 to 400 cm^{-1}. Electronic spectra of the complexes were recorded in $CHCl_3$ solution in a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–200 nm. The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with Bruker 300 MHz instrument using TMS as internal reference.

4.3. Preparation of Schiff base ligands (HL_1–L_3) (**1**–**3**)

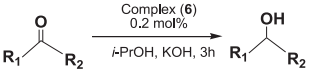
A methonalic solution of salicylaldehyde (or) 3–methoxy salicylaldehyde (or) 2–hydroxy –1–naphtylaldehyde (0.122–0.172g, 1 mmol) and 5–amino–1–methyl–3–phenyl pyrazole (0.173g, 1 mmol) in 20 mL of methanol was stirred at room temperature for a 3 h. The yellow solids were filtered, washed with cooled methanol, dried in air, which was recrystallized from warm methanol.

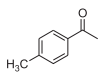
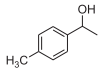
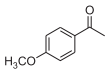
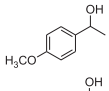
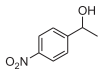
Spectral data for ligands. HL_1 (**1**): Yield: 75%. M. pt. 150 °C. FT–IR (cm^{-1}): 3320 ν(OH), 1620 ν(C=N), 1280 ν(C–O). ^{1}H NMR (300 MHz, $CDCl_3$): 12.37 (s, 1H, OH), 8.73 (s, HC=N), 3.98 (s, 3H, CH_3), 6.59 (s, 1H, CH) 6.96–7.82 (m, Ar–H).

HL_2 (**2**): Yield: 82%. M. pt. 180 °C. FT–IR (cm^{-1}): 3350 ν(OH), 1612 ν(C=N), 1296 ν(C–O). ^{1}H NMR (300 MHz, $CDCl_3$): 12.81 (s, 1H, OH), 8.74 (s, HC=N), 3.97 (s, 3H, CH_3), 3.96 (s, 3H, OCH_3), 6.61 (s, 1H, CH) 6.91–7.82 (m, Ar–H).

HL_3 (**3**): Yield: 90%. M. pt. 195 °C. FT–IR (cm^{-1}): 3399 ν(OH), 1618

Table 5
Transfer hydrogenation of ketones using Ru(η6–p–cymene)(Cl)(L3)] 6a.



Entry	Substrates	Products	Conv.[b] (%)	TON[c]
1			99	495
2			95	475
3			83	415
4			80	400
5			93	465
6			96	480
7			98	490
8			92	460
9			94	470
10			92	460
11			98	490
12			99	495
13			93	465

[a] Conditions: reactions were carried out at 80 °C using 5.0 mmol of ketone, 0.01 mmol catalyst, 0.03 mmol base in 5 mL *i*–PrOH.
Catalyst/substrate/KOH ratio is 1:500:3.
[b] Conversion was determined by GC analysis with authentic samples.
[c] TON = ratio of moles of product formed to moles of catalyst used.

ν(C═N), 1270 ν(C–O). ^{1}H NMR (300 MHz, $CDCl_3$): 14.29 (s, 1H, OH), 9.60 (s, HC═N), 4.00 (s, 3H, CH_3), 6.66 (s, 1H, CH) 7.20–8.22 (m, Ar–H).

4.4. Synthesis of (η^6–p–cymene) ruthenium(II) Schiff base complexes (**4**–**6**)

A mixture containing starting precursor [(η^6–*p*–cymene)Ru(μ–Cl)Cl]$_2$ (0.0918 g; 0.15 mmol), Schiff base ligands (0.088–0.098 g; 0.30 mmol), triethylamine (0.3 mL) in dichloromethane (30 mL) was taken in a clean 100 mL round bottom flask and the reaction mixture was stirred for 12 h at room temperature. The progress of the reaction was monitored using TLC. At the end of the reaction, the solution was concentrated to about 3 mL and hexane was added to initiate the precipitate of orange powder then it was filtered and washed with hexane, and purified using column chromatography.

4.4.1. [Ru(η^6–p–cymene)(Cl)(L_1)] (**4**)

Red-brown solid. Yield: 60%. M. pt. 180 °C. Anal. Calcd for $C_{27}H_{28}N_3ClORu$: C, 59.28; H, 5.12; N, 7.68. Found: C, 59.18; H, 5.02; N, 7.56. FT–IR cm^{-1}): 1605 ν(CH═N), 1328 ν(C–O). UV–Vis λ_{max} (nm): 480, 375, 330. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.0–7.8 (m, Ar–H), 8.6 (s, HC═N), 4.1 (s, CH_3) 3.8 (d, 1H, cymene Ar–H), 4.4 (d 1H, cymene Ar–H), 5.1 (d 1H, cymene Ar–H), 5.4 (d 1H, cymene Ar–H), 2.8 (m, ^{1}H, CH of *p*–cymene), 2.2 (s, 3H, CH_3 of *p*–cymene), 1.2 (dd, 6H, 2CH_3 of *p*–cymene). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 18.3 (CH_3 of *p*–cymene), 21.5, 22.8 (2CH_3 of *p*–cymene), 37.0 (CH_3 of ligand), 30.4 (CH of *p*–cymene), 82.3–86.4 (aromatic carbons of *p*–cymene), 97.5 and 102.0 (quaternary carbons of *p*–cymene), 96.3, 155.4, 167.1 (pyrazole CH_{arom} and C_{arom}), 116.6, 117.7, 120.3, 122.9, 125.3, 127.5, 128.2, 129.4, 132.8, 135.8, 136.8 (CH_{arom} and C_{arom}), 149.9 (C═N), 167.2 (C–O).

4.4.2. [Ru(η^6–p–cymene)(Cl)(L_2)] (**5**)

Orange solid. Yield: 65%. M. pt. 195 °C. Anal. Calcd for $C_{28}H_{30}N_3ClO_2Ru$: C, 58.28; H, 5.20; N, 7.28. Found: C, 58.15; H, 5.10; N, 7.12. FT–IR cm^{-1}): 1600 ν(CH═N), 1331 ν(C–O). UV–Vis λ_{max} (nm): 450, 380, 320. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.4–7.8 (m, Ar-H), 8.7 (s, HC═N), 3.8 (s, OCH_3), 4.0 (s, CH_3), 4.1 (d, 1H, cymene Ar–H), 4.4 (d 1H, cymene Ar–H), 5.3 (d 1H, cymene Ar–H), 5.4 (d 1H, cymene Ar–H), 2.9 (m, ^{1}H, CH of *p*–cymene), 2.1 (s, 3H, CH_3 of *p*–cymene), 1.2 (dd, 6H, 2CH_3 of *p*–cymene). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 18.2 (CH_3 of *p*–cymene), 21.5, 22.8 (2CH_3 of *p*–cymene), 37.0 (CH_3 of ligand), 30.3 (CH of *p*–cymene), 80.8–86.1 (aromatic carbons of *p*–cymene), 97.4 and 102.4 (quaternary carbons of *p*–cymene), 96.3, 152.5, 159.1 (pyrazole CH_{arom} and C_{arom}), 113.8, 116.0, 117.6, 119.2, 125.3, 127.1, 128.1, 132.9 (CH_{arom} and C_{arom}), 149.9 (C═N), 166.9 (C–O).

4.4.3. [Ru(η^6–p–cymene)(Cl)(L_3)] (**6**)

Orange solid. Yield: 80%. M. pt. 210 °C. Anal. Calcd for $C_{31}H_{30}N_3ClORu$: C, 62.36; H, 5.02; N, 7.04. Found: C, 62.08; H, 4.92; N, 6.90. FT–IR cm^{-1}): 1602 ν(CH═N), 1320 ν(C–O). UV–Vis λ_{max} (nm): 460, 365, 335. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.4–7.9 (m, Ar–H), 8.5 (s, HC═N), 4.1 (s, CH_3), 4.4 (d, 1H, cymene Ar–H), 5.2 (d 1H, cymene Ar–H), 5.0 (d 1H, cymene Ar–H), 5.4 (d 1H, cymene Ar–H), 2.8 (m, ^{1}H, CH of *p*–cymene), 2.2 (s, 3H, CH_3 of *p*–cymene), 1.2 (dd, 6H, 2CH_3 of *p*–cymene). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 18.4 (CH_3 of *p*–cymene), 21.3, 22.9 (2CH_3 of *p*–cymene), 37.0 (CH_3 of ligand), 30.5 (CH of *p*–cymene), 81.9–86.6 (aromatic carbons of *p*–cymene), 97.6 and 101.8 (quaternary carbons of *p*–cymene), 96.3, 156.6, 159.6 (pyrazole CH_{arom} and C_{arom}), 119.0, 122.6, 125.1, 126.7, 127.9, 128.9, 133.0, 134.6, 137.4 (CH_{arom} and C_{arom}), 149.9 (C═N), 168.4 (C–O).

4.5. X–ray crystallography

Single crystals of ligand HL_2 (**2**) and complex [(η^6–*p*–cymene) ClRu(L_3)] (**6**) was grown by slow evaporation of the solvent from solution of the respective complex in dichloromethane/n-hexane mixture at room temperature. The data collection was carried out using a Bruker AXS Kappa APEX II single crystal X–ray diffractometer using monochromated Mo–Kα radiation (kI = 0.71073 Å). Data was collected at 296 (2) K. The absorption corrections were performed by the multi-scan method using SADABS software [56]. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS 97) and refined by full–matrix least squares on *F2* using SHELXL 97 [57]. All non–hydrogen atoms were refined anisotropically and the hydrogen atoms in these structures were located from the difference Fourier map and constrained to the ideal positions in the refinement procedure. The unit cell parameters were determined by the method of

difference vectors using reflections scanned from three different zones of the reciprocal lattice. Frame integration and data reduction were performed using the Bruker SAINT–Plus (Version 7.06a) software [58].

4.6. Typical procedure for the catalytic transfer hydrogenation of ketones

In a dry round bottom flask under an atmosphere of nitrogen were placed an appropriate amount of catalyst **4**–**6** (0.01 mmol), (0.03 mmol) of KOH and (5.0 mmol) of ketones in 2–propanol (5 mL) was added and the resulting mixture was refluxed for 3 h. After completion of the reaction, the solvent was removed under reduced pressure. The catalyst was removed by the addition of 15 mL of petroleum ether followed by filtration and subsequent neutralization with dilute HCl. The combined organic fractions were dried with anhydrous Na_2SO_4. Percentage of conversion was determined by GC analysis of the crude mixture and compared with the authentic samples.

Acknowledgments

The authors express sincere thanks to Single Crystal X–ray Diffraction Facility, SAIF Gauhati University, for providing X–ray data collection.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.029.

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